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RPPR Final Report

as of 01-Aug-2018

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Major Goals: The major goals in this research project are several-fold:

- (1) developing a mechano-chemical theory to treat different types of single molecule experiments on biomolecular motors, initially those on F1-ATPase involved in pumping protons and other ions across membranes,
- (2) extending the theory of sum frequency generation experiments for studying the effect of hydrogen bonding at water-organic interfaces on the rates of organic reactions, such as cycloaddition reactions,
- (3) understanding wasteful electron-hole recombination processes involved in photo-excited perovskite materials of solar cell interest, in particular Auger recombination," and
- (4) understanding "fluorescence blinking" of photoexcited CdSe and other semiconductor nanoparticles and the dependence of the rate of energy-wasteful nonradiative recombination of electrons and holes on the size of the nanoparticle.

In topic (1) there are now, in addition to many bulk system experiments, different types of single molecule experiments, such as "stalling" experiments, in which the rotary biological motor is stalled at various angular positions by magnetic tweezers and then after different times allowed to rotate forward or backward to stable positions and relevant rate constants are obtained from those data. There are also "controlled rotation" experiments, in which the motor is rotated at a constant angular velocity that is controlled by magnetic tweezers. To monitor the latter experiments the ATP (adenosine triphosphate) in F1-ATPase studies is replaced by a modified fluorescent ATP. The latter serves to determine whether a site in the ATPase is occupied (the attached dye in the ATP in the ATPase then fluoresces) or not occupied (the ATP and its attached dye are then in solution and there is no fluorescence). From the latter information one obtains rates of various processes occurring in this motor. A goal of our research in this project is to introduce a quantitative theory that we formulated for these kinetics at the molecular level for treating the various reaction steps in these single molecule experiments, and relating them to each other and to bulk experiments, with the aim of obtaining new mechanistic insights into the operation of these biomolecular motors.

In topic (2) we recall that a "sum frequency generation" (SFG) experiment involves two lasers, an infrared laser that excites molecules vibrationally (infrared) and a visible laser that excites them electronically (Raman) via their molecular polarizability, and the two beams are both incident on the surface at a glancing angle. The resulting experimental data are surface sensitive and are seen in an emerging third beam that has no contribution from the body of the (centrosymmetric) interior. The present study on the theory of SFG of water/air and water/organic interfaces was prompted by our earlier articles on the theory of a striking catalytic effect of emulsions on the rates of certain organic cycloaddition reactions ("on-water reactions"), a catalytic effect that we explained in terms of the interaction of the dangling OH bonds at the water interface with the reactants. We note that only a fraction of OH's

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in water molecules at the interface can hydrogen bond to other water molecules, because of the constraints imposed by a largely tetrahedral water structure, so some of the OHs of the surface water molecules are “dangling”. In the “on-water” reactions the “dangling” OHs can serve as catalysts for the type of surface reaction that is dependent on the amount of hydrogen bonding of the transition state relative to that of the reactants. With this chemical reaction background in mind, a goal of our present SFG work is to develop further the theory of the SFG spectra by providing a simple derivation of a theoretical expression for SFG that also clarifies the derivation of the “fast” and “slow” relaxation rate expressions of Wei and Shen and that adds to the comparison of theory and experiment by treating the absolute SFG intensities for the various polarizations of the three beams, rather than mainly their relative SFG intensities.

In topic (3) we are collaborating with the experimentalists in Singapore to interpret experimental results on terahertz spectroscopy and ultrafast fluorescence spectroscopy of perovskites. With these methods the concentration and mobility of the charge carriers, their charge recombination kinetics, and the effect of phase transitions on the polar phonon modes that interact with the charge carriers were studied. The perovskites are of particular current interest in part because of their possible use for efficient solar energy conversion. One goal of our joint research is the study of the energy wasteful electron-hole recombination processes. Since the perovskites are typically studied as films of nanoparticles interparticle surface effects are believed to play a significant role. A second goal is to explore further a standard literature equation, the Drude-Smith equation, used to treat the frequency-dependent electrical conductivity of somewhat distorted systems such as semiconductor films, by incorporating the effect of backscattering of the carriers. In our work on understanding the Drude-Smith equation more fundamentally we are relating it to concepts used to treat backscattering in liquids, namely, diffusion and the velocity autocorrelation function of liquids. They have been treated in the literature by a “memory function” using the nonequilibrium statistical mechanics of liquids. We are using a similar memory function treatment for the semiconductor films to gain added insight into the Drude-Smith equation.

In topic (4) semiconductor nanoparticles, “quantum dots” are extensively explored in the literature for a variety of applications, including photosensitization for solar energy conversion, biosensing, and optical applications. When the typical quantum dots are steadily illuminated they typically undergo a “blinking”, in which they have varying periods of fluorescence and non-fluorescence (bright and dark periods). The dark period is typically interpreted as arising from a charged state of the quantum dot that undergoes a non-radiative recombination (“Auger” recombination) that compete successfully with the radiative rate. In Auger recombination an electron and a hole recombine nonradiatively in a manner that conserves the total energy by simultaneously exciting another electron to a high electronic state in the conduction band of the nanoparticle. Thus far, no theory has successfully explained the quantitative dependence of the Auger rate on the particle radius, a rate that typically varies approximately as the third power of the radius. One goal of this study is to formulate such a theory and, in the process, address the question as to whether quantum states of the charges in the core of the quantum dot or surface quantum states of the charges can best explain this dependence on this power on the size of the quantum dot.

Accomplishments: For topic (1) papers were published on the theory of the single molecule experiments on a biomolecular motor, F1-ATPase, and on the comparison with the available experimental data, in the journals *Proceedings of the National Academy of Sciences* (2015, 2016, 2017), *Quarterly Reviews of Biophysics* (accepted 2017), *Modern Physics Letters* (2016), and in two book chapters (accepted 2016, 2017). The data treated initially in PNAS were on the ATP binding step in the series of reaction steps, and it successfully explained the existing data. In a second PNAS paper the theory was applied to controlled rotation single molecule experiments. In the latter the data from stalling and bulk experiments were used to predict the results of the controlled rotation experiments, using no adjustable parameters, in the range of rotation angles where the two single molecule experiments overlap. Good agreement was found between experiment and theory for the various angle-dependent rates. This comparison is illustrated in Figure 1 of the Additional Information section of this Final Report. In a third paper in PNAS we extended the studies so as to include the successive series of processes involved in the full rotation of the F1 ATPase. ATP binding, ATP hydrolysis, and ATP release. The analysis permits one to interpret previous experimental data on the full rotation that previously could not be interpreted. We are now collaborating with the lead author in the experiments to interpret the data using this new theoretical study.

In the studies in topic (2) we expanded the theory of sum frequency generation (SFG) and its application to some existing experiments at a water interface: in this work a goal was to obtain absolute values of the SFG absorption intensities, drawing upon and extending a method of Wei and Shen, who utilized experimental results on infrared transition dipole moments and on Raman transition moments. The product of the two appears in the theoretical SFG expression as a “hyperpolarizability” of the system. We showed analytically how the fast and slow motion expressions of Wei and Shen for SFG could be derived from a more general expression, and in the process

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corrected their original theoretical derivation. Implementation of the theory involves the dependence of the OH vibration frequency of a water molecule on the electric field due to its neighboring water molecules both near and far, which in turn depends upon the distances between the OH of this water molecule and its neighbors. For the latter we utilized results in the literature of SFG and other experiments. We used classical trajectories to follow the translational and rotational motions of the water molecules in the system, and from the results calculated the SFG absorption spectra from the relevant theoretical time-correlation function, a time-correlation of the polarizability of the system at time $t=0$ and the dipole moment of the system at time t . Reasonable agreement between theory and experiment on the absolute intensities was obtained for the polarization combination of the three laser beams with the largest intensity. A comparison of theory and experiment is given in Figure 2 in the Additional Information section of this Final Report. A remaining issue to be resolved is what values to use for the dipole and polarizability transition moments that appear in the theory. Wei and Shen used the gas phase values and tentatively we used those values, while others have used that for bulk water or ice, but more appropriate would be an OH that, like an OH protruding from a surface water molecule, is free (not hydrogen bonded) but is also hydrogen bonded to a neighboring water molecule, for example that of an end OH in a water dimer. We are currently exploring this question and how to utilize infrared and Raman intensity data on water dimers for this purpose. We are also interacting with a UC San Diego electronic structure theorist, Professor Francesco Paesani, in the latter calculation.

For topic (3) we studied the Drude-Smith equation for the frequency-dependent conductivity of semiconductors, an equation widely used in the literature to treat the frequency dependent conductivity of somewhat disordered materials. In this study we used a memory function formalism, and provided additional insight into the former. A paper on this work is in preparation. In collaboration with a group from Singapore we studied the terahertz spectroscopy of the phonon modes of perovskite, a study in which there were no electron and hole charge carriers (no photoinduced production of them), and so the only response was that of the polar vibrations of the material. The results showed reasonable agreement with the theoretical calculations of the terahertz spectrum calculated by another group. We also studied the terahertz spectroscopy where there is instead a photo-induced production of charged carriers. Experimental results on the concentration of the carriers and their mobility were obtained by the application of the Drude-Smith expression. We also studied and published papers on the absorption spectrum of perovskites and on the effect of phase transitions on the phonon spectrum, quantities related to the application of perovskites to solar energy conversion.

For the study in topic (4) we calculated the electronic structure of the quantum dot (QD) using a "tight binding" method and a quantum theory of rate processes to calculate the Auger recombination rates for CdSe quantum dots. Eigenvectors and eigenvalues were obtained for the one-electron states of the conduction band and those of the valence band of the quantum dot. The results for the calculated Auger rates had too large a dependence on the power of the radius of the QD, compared with the experimental results. In this study the quantum states of the QD in the computation were bulk states in the quantum dot. We are now exploring alternative explanations and have modified the calculation so as to include an Auger recombination that involves surface states of the quantum dot.

Training Opportunities: Two members of the group, Drs. Yun-Hua Hong and Wei-Chen Chen, have used their training in basic theoretical research and computation to obtain positions in the industry, one in the financial sector and the other in the property management sector. Dr. Sandor Volkan-Kacso has now published extensively in a basic research field that combines mechanical and chemical concepts, the field of biomolecular motors. He has learned much in the formulation of theories and in their comparison with experience, and is now using this background in his applications for academic positions.

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Results Dissemination: Articles were published in scientific journals, as listed elsewhere in this report, and the research was described in talks at various symposia and other international meetings, listed below. They include talks at scientific meetings and talks of a more educational nature to high school and college students.

List of Talks:

Lecture, Ventures in science, theory and experiment, University of Granada, Spain, September 2014

Opening lecture, Single molecule intermittent fluorescence studies of quantum dots and in initial steps in dye sensitized solar cells, International Conference of Fundamental Processes in Semiconductor Nanocrystals Oxford, United Kingdom, September 2014

Honorary Chairman and Plenary Lecture, Single molecule intermittent fluorescence studies of quantum dots and in initial steps in dye sensitized solar cells – examples of electron transfers and diffusion, 19th International Workshop on Quantum Systems in Chemistry, Physics and Biology, Taipei, Taiwan, November 2014

Plenary Lecture, Electron transfer reaction theory in chemistry – from the isotopic exchange reactions of the 1940s and 1950s to the modern solar energy conversion era, Global Young Scientists Summit, Singapore, January 2015

Lecture, Early steps in polyelectrolytes study and a leap into the electron transfer theory, Polyelectrolytes in Chemistry, Biology and Technology Workshop, Singapore, January 2015

Plenary Lecture, Electron transfer theory in single molecule studies of intermittent quantum dots and in initial steps in dye sensitized solar cells, The 15th International Congress of Quantum Chemistry, Beijing, China, June 2015

Lecture, Electron transfer theory in single molecule studies of intermittent fluorescence of quantum dots and in initial steps in sensitized solar cells, Nobel Laureate Meeting, Lindau, Germany, July 2015

Lecture, Electron transfers: From simple isotopic exchange reactions to the single molecule era, Multiscale Modeling of Complex Molecules and Life Processes: A Symposium Honoring and Celebrating Dr. Arie Warshel, University of Southern California, November 2015

Lecture, Rates, equilibrium constants and brønsted slopes in F1-ATPase single molecule imaging: Experiments and a theoretical approach, 4th International Workshop on Solar Energy for Sustainability "Photosynthesis and Bioenergetics," Singapore, March 2016

A Talk on Scientific Research, deToledo High School Science Academy Colloquium, West Hills, California, April 2016

Lecture, The energy-rich molecule ATP studied in single molecule experiments: theory, predictions, and tests for the different experiments on the enzyme F1-ATPase, Baku International Humanitarian Forum, Azerbaijan, September 2016

Lecture, Theory of single molecule experiments of F1-ATPase: Predictions, tests and comparison with experiments, 24th Solvay Conference on Chemistry "Catalysis in Chemistry and Biology," Brussels, Belgium, October 2016

Lecture, A Chemical-Mechanical Theory of a Biomolecular Machine, F1-ATPase: Predictions, Tests and Comparison with Single Molecule Experiments, 9th Asian Photochemistry Conference, Singapore, December 2016

Lecture, Six decades of Marcus Theory, Nobel Laureate master class lecture, International Science Youth Forum, Singapore, January 2017

Lecture, Quantum mechanics and chemical reaction rates, 1928 and counting, Conference on 90 Years of Quantum Mechanics, Singapore, January 2017

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Honors and Awards: Induction into the Alpha Chi Sigma Hall of Fame; Charlottesville, Virginia (2014)

Chairman, International Peer Review of the College of Chemistry and Molecular Engineering, Peking University, China (2015)

Honorary Editor of the Springer Book Series PROGRESS IN THEORETICAL CHEMISTRY AND PHYSICS (2016)

Electrochemical Society Masters Film Interview; Pasadena, California (2016)

E&S Magazine "No Rest for a Nobelist: Rudolph A. Marcus" Film Interview; California Institute of Technology, Pasadena, California (2016)

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Staff Scientist (doctoral level)

Participant: Wei-Chen Chen

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Staff Scientist (doctoral level)

Participant: Yun-Hua Hong

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Staff Scientist (doctoral level)

Participant: Zhaoyan Zhu

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Sandor Volkan-Kacso

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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as of 01-Aug-2018

BOOKS:

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Authors: Editors Majed Chergui, Rudolph A. Marcus, John Meurig Thomas, Dongping Zhong
Editor:
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Comparison of theory and experiment for ATP binding in F₁-ATPase

The stalling and controlled rotation experiments are complementary provide the θ -dependent rate constants and equilibrium constants for the steps, such as ATP binding. In the former, a fluorescent species, Cy3-ATP and Cy3-ADP, is used instead of ATP and ADP. We have shown [Volkán-Kacsó, S. & Marcus, R. A. (2016), *Proc. Natl. Acad. Sci. USA*, **113**, 12029–12034; Volkán-Kacsó, S. & Marcus, R. A. (2017), *Proc. Natl. Acad. Sci. USA*, **114**, 7272–7277] that the theory provides a symmetric expression for the rate constant versus rotor angle dependence,

$$\begin{aligned} kT \ln k_f(\theta) &= kT k_f(\theta_c) + (1/2 + \Delta G_0^0 / 2\lambda) \Delta \theta_r - (\Delta \theta_r)^2 / 4\lambda, \\ kT \ln k_b(\theta) &= kT k_b(\theta_c) + (-1/2 + \Delta G_0^0 / 2\lambda) \Delta \theta_r - (\Delta \theta_r)^2 / 4\lambda, \end{aligned} \quad (1)$$

where $\Delta \theta_r = \kappa(\theta_f - \theta_i)(\theta - \theta_c)$ and $\theta_c = (\theta_i + \theta_f)/2$; θ_i and θ_f are the initial and final dwell angles; ΔG_0^0 and λ are the standard free energy and “reorganization energy” of the reaction step; and κ is the spring constant of the structural linkage between the conformational change associated with the step and the rotation of the motor shaft. The quadratic term is small in the case of the ATP binding step (less than 8% contribution). We note that for the equilibrium constant this dependence is predicted to be exponential,

$$kT \ln K(\theta) = kT \ln K(\theta_c) - \kappa(\theta_f - \theta_i)(\theta - \theta_c). \quad (2)$$

The $\ln K(\theta)$ seen in Eq. 2 to be linear in θ , in agreement with the experimental data. With data from other ensemble and single molecule experiments the theory was used to predict independent single-molecule experimental. In particular, the stalling data, supplemented by ensemble data, was used to predict, using Eqs. 1 and 2, the rate constants in the controlled rotation experiments with no adjustable parameters. The comparison is given in Fig. 1, in the θ -range of overlap. Good agreement was found between these experiments and our calculations, seen there, where the points (symbols) are experimental and the solid curves theoretical data.

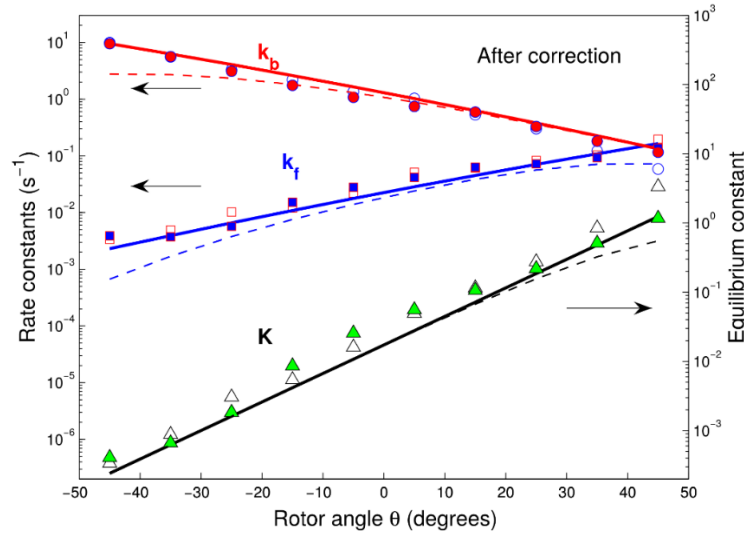


Fig. 1. Corrected binding and release rate and equilibrium rate constants versus θ angle for Cy3-ATP in the presence (solid squares, circles and triangles) and absence of Pi (open symbols) in solution [Volkán-

Kacsó, S. & Marcus, R. A. (2016), *Proc. Natl. Acad. Sci USA*, **113**, 12029–12034]. The experimental data from controlled rotation experiments corrected for missed events (and an error due to replacing the time spent in the empty state by total time of a trajectory) are compared with their theoretical counterparts (solid lines). Dashed lines show the data without corrections.

Comparison of theory and experiment for the largest SFG component

In the attached figure, taken from a draft of the paper we have prepared, a comparison of theory and experiment with no adjustable parameters is given for the polarization component SSP that has the largest intensity. Considering the approximations that are made the agreement is surprisingly good, better than a factor of two for the integrated intensity. For the transition dipole moments and the transition polarizabilities of the surface H₂O molecules the taken from the gas phase H₂O are used, following the work of Wei and Shen. However, it would be more appropriate to use values more appropriate to an H₂O that has one OH not hydrogen bonded and the other OH hydrogen bonded. We are currently exploring this possibility, needed to obtain agreement for the polarizations PPP and SPS that

Here, SSP denotes that both the sum frequency and the visible beams are s-polarized and the P denotes that the infrared beam is P polarized, that is, that the electric field vector is perpendicular to the surface. The experimental ratios for the integrated intensities are PPP:SSP and SPS: SSP are approximately 0.1 and 0.03 respectively, so SSP is clearly the dominant polarization combination in the spectra.

The SFG Spectrum comparing experiment and theory for the SSP polarization combination using no adjustable parameters is given in Fig.2

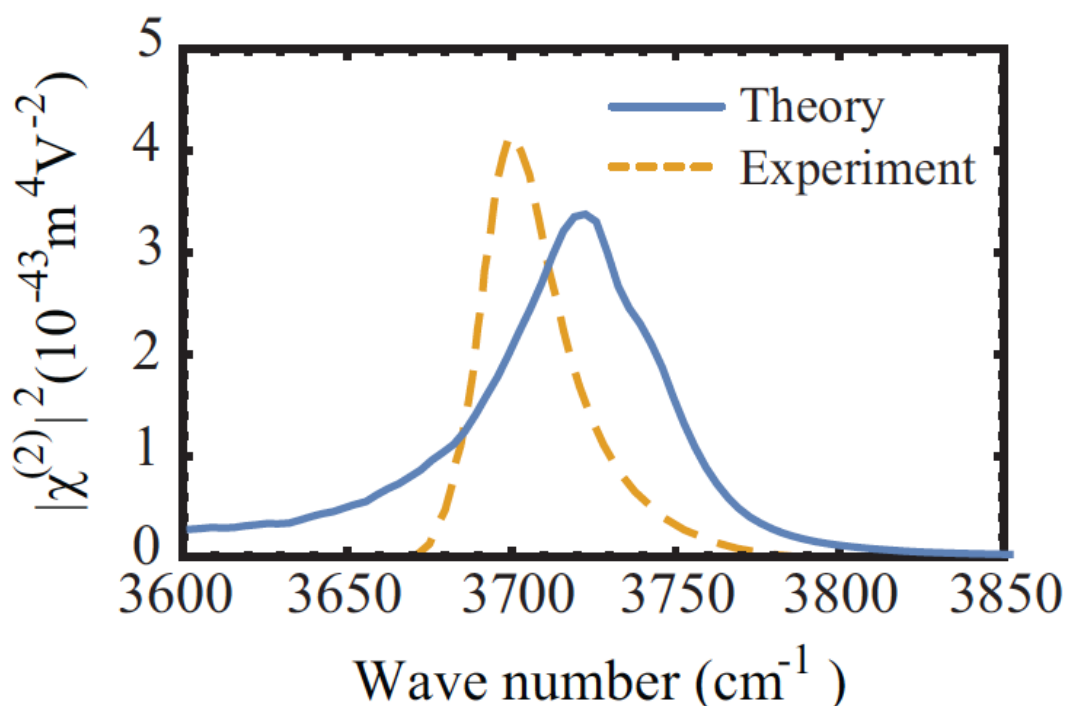


Fig.2 Comparison of experimental and theoretical SFG spectrum for the SSP combination of polarizations

W911NF1410351 – Novel Surface Phenomena
Additional Comment to Final ARO Report
PI: Rudolph A. Marcus

As requested by Dr. Mantz, several additions to the final ARO report 6/23/14 to 6/22/17 have been made and are given below.

Biomolecular motors. A principal goal of this work is to formulate a theory that treats the detailed relation between the mechanical motion of the rotary biological motor $F_1 F_0$ ATP Synthase and its chemical reactions. The experiments that we treat are single molecule experiments that are providing new detailed information on the mechanism of these motors. The chemistry that the motor couples to is the hydrolysis of adenosine triphosphate (ATP), associated with the pumping of protons and other ions across biological membranes, and with the reverse process of using transmembrane ion gradients to generate ATP, a biological "energy source", from adenosine diphosphate (ADP) and inorganic phosphate (Pi).

Our central idea is to predict the results of one type of single molecule experiment on these motors from independent results on another type of experiment, using largely analytical theory with no adjustable parameters. If the theory is an appropriate predictor the predicted and observed experimental results will agree, and in this way a unified approach can be used to understand and treat different experiments.

In the single molecule experiments for the enzyme $F_0 F_1$ ATP Synthase, the water accessible F_1 , and a central stalk are separated from the membrane-bound F_0 and attached to a surface such that the stalk can rotate while the F_1 is held fixed. Using optical methods the rotation of the stalk can be followed in real-time, while using magnetic tweezers the rate of rotation of the stalk can be controlled. Further, the rotating stalk can be stalled at various angles of the rotor, angles between the resting angles ('dwell' angles). Release of the stalling permits the system to go to the forward dwell angle or revert to the previous one, and the angle-dependent rates of reaction going forward or reverting can both be measured. Again, using a fluorescent probe the occupancy of the different subunits (the three 'beta' subunits) of the F_1 can be followed in real time and angle-dependent rate constants obtained from them.

To relate these different kinds of experimental data to each other we introduced a chemo-mechanical theory in which there are chemical and mechanical (torsional) contributions to the free energy of the system at each rotor angle and to the free energy of activation for the reaction at that rotor angle. In this mechanism these species enter and others leave the various beta subunits in a systematic way. The size of the openings in the clefts in the three beta subunits into which these species (ATP, ADP, Pi) enter and leave depend on the extent of interaction of the species with the clefts and it in turn depends on the opening and closing of the clefts. The latter is coupled to the rotor angle because of the rotational asymmetry of the central stalk and its contact with the asymmetric subunits. In this system the rates of the various processes tend to be exponentially dependent on the rotor angle for

energetic reasons.

We applied the theory to the single molecule studies of the angle-dependents rate constants, treating initially the ATP binding and the ATP release. The predictions of the different angle-dependent rates agreed well with the experimental results with no adjustable parameters, the predictions being based on other experiments that are independent of those treated. A plot of these results illustrating this agreement was given in the appendix of the previously submitted ARO final report.

This work was followed up with an article that showed how successive convoluted steps in the overall process could be treated. This latter work will permit the treatment of previously untreated experimental data that are now being treated in our current research.

Sum frequency generation theory

'On-water catalysis' is a remarkable phenomenon discovered by Sharpless and coworkers in 2005 in which a particular organic cycloaddition reaction was catalyzed from a half life of 40 hours to one of 10 minutes when the two reacting organic liquids were mixed with excess water, forming an emulsion with considerable surface area. We offered an explanation of the catalysis in terms of dangling OH bonds at the water-organic interface, dangling because it is impossible for the water molecules at the surface to have their usual tetrahedral coordination without some of the OHs dangling at the surfaces unbonded to other H₂Os. The catalysis should occur in our theory when the transition state of the organic reaction is more hydrogen bonded to the surface dangling OHs than are the two reactants. Numerical computations using density functional method supported this explanation.

A tool for studying the nature of the OHs at a water-air or water-organic interface is sum frequency generation. In this method an infrared laser beam and a visible laser beam are incident on the surface at a glancing angle and the frequency-dependent intensity of the outgoing combination beam is measured. Because of the nonlinear nature (two electric fields, rather than one) the data are dependent on the behavior at the surface with no contribution from the bulk of the liquid, for the typical case of a centro-symmetric nature of the body of the liquid.

Pioneering work in this field was done by Shen and coworkers. The three polarization combinations studied experimentally by them in their study of the air water interface were SSP, SPS, and PPP. In SSP the first S denotes that the electric field vector of the outgoing combination beam is parallel to the surface. The second S denotes that the incident visible beam has its electric field vector also parallel to the surface, and the P in SSP denotes that the incident infrared beam has its electric field vector perpendicular to the surface. Since the dangling OH tends to be roughly perpendicular to the surface it is clear that SSP should have the strongest intensity, and it does.

For the theoretical expressions for the three polarization combinations two of them are simple one-term expressions (the SSP and SPS), while the PPP expression has 4 terms with

partial cancellations in sign and so more difficult to interpret in physical terms. There has since been extensive theoretical work, comparing with the experimental results for the different polarization combinations of the three laser beams. Typically relative values of SFG intensities for the various polarization combinations are computed instead of absolute intensities. We were curious as to whether it would be possible to obtain reasonable agreement for absolute intensities, with no adjustable parameters, using data on absolute intensities of the infrared and Raman spectra of water molecules. Here, some choice was needed. The dangling OH SFG peak at $\sim 3700\text{ cm}^{-1}$ is absent in Raman and infrared spectral of bulk water and for bulk ice, since they have no dangling OH bonds. So, we could not use that source of information.

Another possibility was to use the data for gas phase water molecules since they do have this $\sim 3700\text{ cm}^{-1}$ peak. (An improved choice, would be to use data for an end OH on water clusters, since it would better represent the neighborhood of a dangling OH, but it would require a very detailed spectral analysis.) So, using the IR and Raman data for gas phase water we obtained agreement to a factor of 2 for the polarization contribution with the largest intensity. We regard this agreement as quite reasonable. We obtained results for three polarization combinations, with reasonable agreement.

As a side issue we were interested in seeing whether the theoretical expression for SFG, normally obtained by perturbation theory could also be obtained by the so-called relaxation method sometimes used for one-laser systems. Here, we adapted the method to the nonlinear two-laser system involved in SFG, and obtained the desired result for the SFG spectrum.

Semiconductor quantum dot blinking and effect of radius on Auger rate

The intermittent fluorescence of semiconductor quantum dots has been the subject of numerous experimental and theoretical investigations. During this intermittent fluorescence there are dark periods, where there is no fluorescence, and bright periods where there is. There is evidence from the Nesbitt group that at higher incident light intensities there is an enhanced tendency towards dark periods results believed to be due to the formation of biexcitons at higher concentration of excitons (an electron-hole pair) at the higher incident light intensities. These excitons in a biexciton can interact, causing the electron in one exciton to go high into the conduction band and the electron of the other exciton to go into a hole in the valence band, so satisfying the law of conservation of energy. This process is an example of an Auger process. Kinetically this interaction of the two excitons behaves like a bimolecular reaction with a rate that is proportional to the square of the light intensity.

In an examination of the literature in the Caltech PhD thesis of Yun-Hua Hong a list was made of the experimentally observed dependence of the Auger lifetime on the volume of the quantum dot for different quantum dots. Typically the lifetime was approximately inversely proportional to the volume of the QD, a behavior again expected for a simple bimolecular process. In the Nesbitt work the QD size was not studied and so there is no information on this size effect from the latter. Using electronic structure theory, such as

tight binding theory, the calculated dependence of Auger lifetime had too high a dependence of Auger lifetime on the QD volume, and thus far in the literature no one seems to have overcome this problem. There is clearly a need for further study, particularly on surface defects and their potential role in these processes.